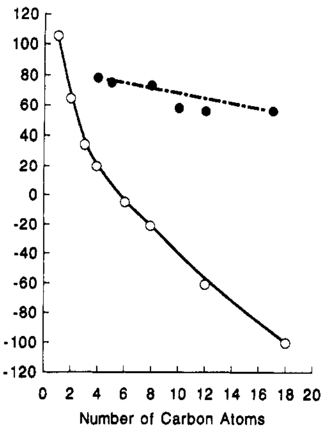

Figure 1. T_g versus number of carbon atoms in the *n*-alkyl (○) or alicyclic (●) side group. Data for T_g of poly(*n*-alkyl methacrylates) are taken from ref 9. The dashed line for the ring materials and the solid curve for the *n*-alkyl materials are intended to guide the eye; i.e., they are not statistical fits to the data.

cyclic rings also are less flexible (have fewer conformations available to them) than the corresponding *n*-alkyl derivatives. Furthermore, the carbon linked to the carbonyl for alicyclic polymethacrylates may be viewed as disubstituted. It is interesting, therefore, to compare the T_g of PCBM (78 °C) with that of poly(*sec*-butyl methacrylate) (T_g = 60 °C[10]), which has the same degree of substitution. The *sec*-butyl group is bulkier than the cyclobutyl ring, but the latter is more rigid and thus imparts the higher T_g. On going to the bulky and rigid ("trisubstituted") *tert*-butyl group, a still higher T_g of 118 °C[10] is found.

In summary, the effects of both internal plasticization and bulkiness of the ring appear to influence the T_g of alicyclic polymethacrylates. The observed slight decrease of T_g with ring size shows that these two effects roughly offset one another for the polymethacrylates of this work.

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Registry No. PCBM, 118420-90-9; PCPM, 28298-90-0; PCOM, 28298-92-2; PCDM, 64328-83-2; PCDDM, 64328-84-3; PCHDM, 127333-31-7.

Oxygen Enrichment by a Langmuir–Blodgett Film of Poly(*N*-dodecylacrylamide) on Porous Aluminum Oxide

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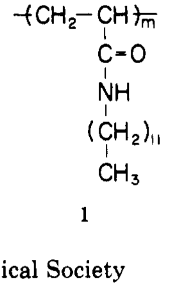
Introduction

The development of permselective membranes is important for the establishment of energy-saving processes. It is well-known that the Langmuir–Blodgett (LB) technique provides uniform ultrathin films with well-defined molecular orientation.[1,2] The use of LB multilayers for gas separation has been desired, but there have been only a few studies: Rose and Quinn,[3] Gaines and Ward,[4] and Albrecht et al.[5] have measured gas permeability through LB films such as barium stearate and cadmium arachidate. They found only a decrease in gas flux by the LB films. Effective gas separation was not achieved. Higashi et al. have reported the selective permeation of oxygen by LB films consisting of fluorocarbon amphiphiles.[6,7]

Some of the present authors[8–12] have recently shown that *N*-alkyl-substituted acrylamides and preformed poly(*N*-dodecylacrylamide) give stable uniform LB multilayers. We have attempted to use these polymer LB films for separation processes. In this note, it is demonstrated that the LB film of poly(*N*-dodecylacrylamide) (PDDA (1)) deposited on a porous aluminum oxide acts as a permselective membrane for oxygen.



$$\begin{array}{l} -\!\!\!\left(\mathrm{CH_2-CH}\right)_{\overline{m}} \\ \qquad\quad \mathrm{C{=}O} \\ \qquad\quad \mathrm{NH} \\ \qquad\quad \mathrm{(CH_2)_{11}} \\ \qquad\quad \mathrm{CH_3} \end{array}$$

1

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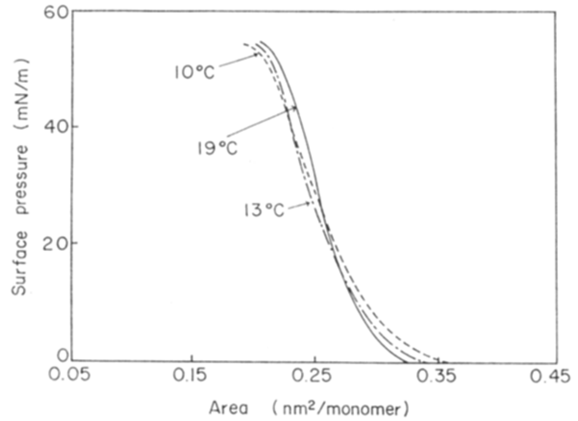

Figure 1. Surface pressure–area isotherms of PDDA monolayer at various subphase temperatures.

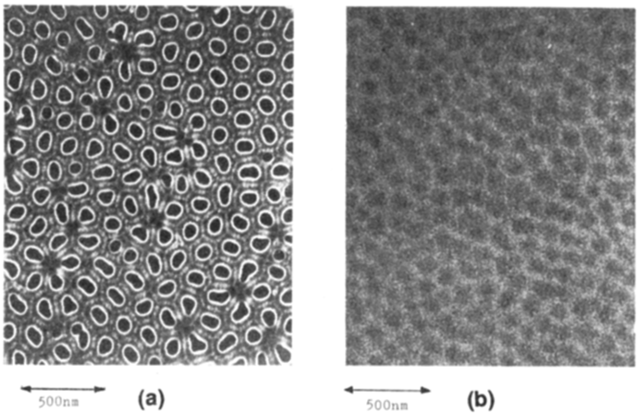

Figure 2. Electron micrographs of the surface of bare porous aluminum oxide (a) and the support covered with PDDA LB film (b).

Experimental Section

The preparation of PDDA has been described elsewhere.[8,11,12] The number-average molecular weight of the PDDA was 3.6 × 10^3. The measurement of surface pressure–area isotherms and the deposition of the polymer monolayer were carried out with an automatic Langmuir trough (Kyowa Kaimen Kagaku HBM-AP).

The porous support used was anodic aluminum oxide film that had a well-defined pore structure characterized by the straightness and narrow size distribution of the pores. The oxide film was prepared by the same method as described in previous work.[13] The thickness of the oxide film was 50 μm. The average pore size was determined to be ca. 100 nm by means of the gas permeation method, and the pore density was 5.9×10^9 cm^{-2}.

The gas permeation measurements were carried out with a high-vacuum method described elsewhere.[13]

Scanning electron micrographs were taken with a Hitachi H800 electron microscope.

Results and Discussion

A chloroform solution of PDDA was spread on the surface of water. Surface pressure–area isotherms with a steep increase of the surface pressure and a high collapse pressure were obtained, indciating the formation of the stable condensed PDDA monolayer (Figure 1). The monolayer on the water surface could be transferred onto the porous aluminum oxide support at a surface pressure of 40 mN/m and 19 °C. Because of the hydrophilicity of the aluminum oxide surface, no deposition at the first downstroke was observed. At the subsequent upstroke and downstroke, however, Y-type deposition with a transfer ratio of 1.0 (+0.1) was observed. The SEM photograph of the surface of the LB film with 49 layers on the porous aluminum oxide is shown in Figure 2. The picture shows that the polymer LB film covers all the surface of the support, and the pores can be dimly seen through the film (Figure 2b). The thickness of the PDDA monolayer has been obtained as 1.8 nm.[12] From the number of deposited layers (49), the thickness of the LB film is estimated to be 88.2 nm. The value is almost in agreement with the thickness observed in the cross-sectional view of the LB film by electron micrography.

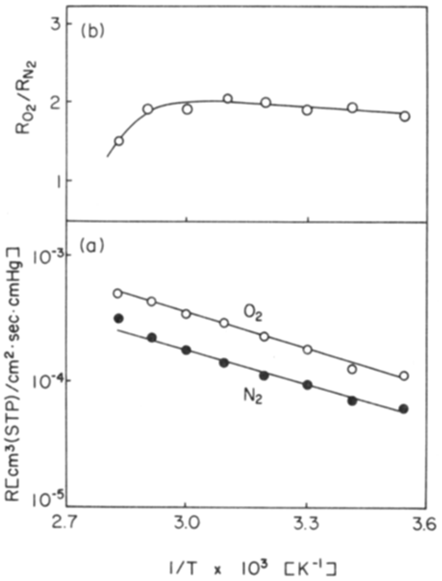

Figure 3. Permeation rates of oxygen and nitrogen at various temperatures (a) and the separation factors (b).

Gas permeation rates through the composite membrane of the LB film and the aluminum oxide support were measured for oxygen and nitrogen gases by means of a high-vacuum method.[13] Figure 3 shows the temperature dependence of the permeation rates of oxygen and nitrogen gases and the separation factors. It is apparent that the permeation rate of oxygen is higher than that of nitrogen gas. The separation factor was obtained as ca. 2.0 at temperatures from 10 to 70 °C. Although the separation factor is slightly smaller than that for reported fluorocarbon polyion complex LB film,[6,7] the permeation rate of oxygen, R (cm^3 (STP) cm^{-2} s^{-1} $cmHg^{-1}$), was in the range 10^{-3}–10^{-4} (from 10 to 70 °C), which is ca. 10 times higher than that for the fluorocarbon LB film. The apparent activation energies for oxygen and nitrogen permeation were 5.8 and 5.7 kcal/mol, respectively. It has been reported that the gas permeation rates through the aluminum oxide support are controlled by a Knudsen diffusion mechanism;[13] thus, the oxygen permeation rate is slightly lower than the nitrogen permeation rate. Therefore, the oxygen enrichment in Figure 3 is attributable to the interaction of the gases with the LB film. That an effective oxygen enrichment can be achieved with the thin PDDA LB film with only ca. 88-nm thickness indicates that PDDA polymer has an excellent property forming a relatively defect-free and uniform polymer LB film. Moreover, it is noteworthy that the polymer LB film can work at even 70 °C as a permselective membrane. The layer structures of usual long alkyl fatty acid LB films are known to be broken at ca. 50 °C.[2a] The thermal stability may be due to the polymer form.

In conclusion, the present results show that the PDDA LB multilayer is a potential candidate for an effective permselective membrane for oxygen.

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Registry No. 1, 33827-81-5; aluminum oxide, 1344-28-1; oxygen, 7782-44-7; nitrogen, 7727-37-9.

Polymeric Blocked Isocyanates by Reductive Carbonylation of Nitropolystyrene

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Polymeric isocyanates and their precursors of controlled molecular weight and degree of functionality are important building blocks in powder coating formulations.[1-3] Metal carbonyl induced reductive carbonylation of nitroaromatics has been explored as a phosgene-free route for the preparation of isocyanates and blocked isocyanates.[4-6] Application of carbonylation methodology to nitro-substituted oligomers or polymers represents a novel route to polymeric cross-linkers with no intermediacy of phosgene or low-molecular-weight isocyanates. Besides, the information available on the chemical reactions of polymers suggests that polymeric substrates may be useful in distinguishing homogeneous and heterogeneous catalysts.[8,9] We report here the use of the $Ru_3(CO)_{12}/NEt_4^+Cl^-$ system for the reductive carbonylation of nitro-substituted polystyrene.

A typical experimental protocol for the reductive carbonylation of nitropolystyrene (**2**) is as follows.[5,6] Polystyrene (**1**) was nitrated with HNO_3/H_2SO_4 at 0 °C, and the degree of nitration was estimated by nitrogen analysis.[10] Nitropolystyrene (0.5 g) (elemental analysis: C, 56.24 (64.4) N, 9.03 (9.39); H, 4.69 (4.27) ($n = 1$)) in toluene/methanol (25 mL) was allowed to react with CO (450 psi) at 160–170 °C in a 200-mL autoclave in the presence of $Ru_3(CO)_{12}$ (0.156 mmol) and $NEt_4^+Cl^-$ (1.09 mmol) for 6 h. The proposed reaction pathway (I) is presented in Figure 1.

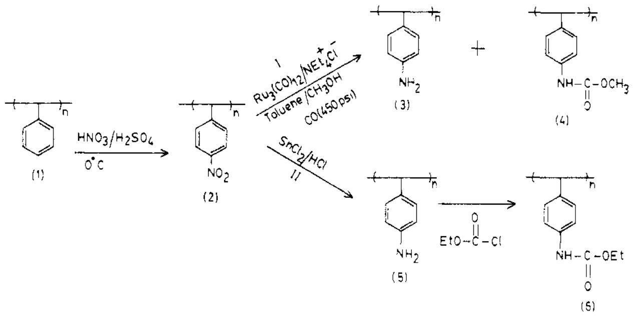

Figure 1. Synthesis of polymer-bound blocked isocyanates.

Table I
$Ru_3(CO)_{12}/NEt_4^+Cl^-$-Induced Carbonylation of Nitropolystyrene

			selectivity,[a] %		
substrate	catalyst	conv, %	Ⓟ–NCO	Ⓟ–NH_2	Ⓟ–NHCOOR
Ⓟ–NO_2[b]	$Ru_3(CO)_{12}/NEt_4^+Cl^-$ toluene/methanol	100		60	40
Ⓟ–NO_2[b]	$Ru_3(CO)_{12}/NEt_4^+Cl^-$ acetonitrile/methanol	90		70	25
Ⓟ–NO_2[b]	$Ru_3(CO)_{12}$ toluene/methanol	80		80	
Ⓟ–NO_2[b]	$Ru_3(CO)_{12}$ acetonitrile	100	trace	80	
Ⓟ–NO_2[c]	$Ru_3(CO)_{12}/NEt_4^+Cl^-$ toluene/methanol	100		50	50
Ⓟ–NO_2[c]	$Ru_3(CO)_{12}/NEt_4^+Cl^-$ acetonitrile/methanol	95		60	40

[a] Experimental conditions: temperature, 170 °C; pressure, 450 psi of CO; time, 6 h. Percentages of products refer to weight fractions of the polymers. [b] Polystyrene M_w = 60 000 and degree of substitution $n = 1$. [c] Polystyrene M_w = 10 000 and degree of substitution $n = 0.5$.

$Ru_3(CO)_{12}$ has been found to be an effective catalyst in toluene/acetonitrile/methanol at 170 °C and 400–450 psi of CO for the reductive carbonylation of nitropolystyrene. Table I summarizes the results of carbonylation experiments under various conditions. In most cases, complete conversion was achieved with the disappearance of nitro groups (1535, 1350 cm^{-1}). Typically, the reaction yielded a mixture of **3** and **4**. The molecular weight and degree of nitration were found to be critical in achieving good solubility of the samples and influenced conversions and selectivities. In general, an increased level of nitration resulted in poor solubility of the polymer and lower selectivities. The conversions and selectivity were dependent on the solubility of the nitropolymers, presence of cocatalyst, and the nature of solvent mixture. Removal of $NEt_4^+Cl^-$ and ROH resulted in total conversion to **3**. Carbamate formation was detected by the presence of a carbonyl peak at 1720 cm^{-1}. It was

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